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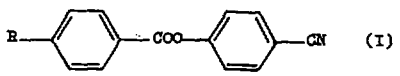
(19)

(54) P-ALKYL BENZOIC ACID p'-CYANO PHENYL ESTERS AND THEIR USE IN LIQUID CRYSTALS

(71) We, F. HOFFMANN-LA ROCHE & CO., AKTIENGESELLSCHAFT, a Swiss Company of 124—184 Grenzacherstrasse, Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to liquid crystalline esters. More particularly, the invention is concerned with liquid crystalline esters, a process for the manufacture thereof, nematic mixtures for electro-optical purposes containing said esters and a process for the production of nematic mixtures. The invention is also concerned with dielectrics for electro-optical purposes and with the production thereof.

The liquid crystalline esters provided by the present invention are compounds of the general formula



(I)

wherein R represents a straight-chain alkyl group containing 4 to 8 carbon atoms.

The compounds of formula I possess, in the liquid crystalline state, a positive anisotropy of the dielectric constants ($\varepsilon_{//} > \varepsilon_{\perp}$, $\varepsilon_{//}$ signifying the dielectric constant along the longitudinal axis of the molecule and $\varepsilon_{\perp}$ signifying the dielectric constant perpendicular thereto).

In an electric field the nematic liquid crystals provided by the present invention orient themselves (because $\varepsilon_{//} > \varepsilon_{\perp}$) with the direction of their largest dielectric constant, (i.e. with their longitudinal axes) parallel to the field direction. This effect is employed, inter alia, in the interaction between embedded molecules and liquid crystalline molecules (guest-host interaction) described by J. H. Heilmeier and L. A. Zanoni [Applied Physics Letters *13*,91 (1968)]. A further interesting application of the dielectric field orientation exists in the rotation cell discovered by M. Schadt and W. Helfrich [Applied Physics Letters *18*, 127 (1971)].

This electro-optical rotation cell is essentially a condenser having transparent electrodes whose dielectric is formed from a nematic substance with $\varepsilon_{//} > \varepsilon_{\perp}$. The longitudinal axes of the molecules of the liquid crystal are arranged in twisted form between the condenser plates in the fieldless state, the twisting structure being defined by the given wall orientation of the molecules. After the application of an electrical potential to the condenser plates, the molecules adjust themselves with their longitudinal axes in the field direction (i.e. perpendicular to the surface of the plates), whereby linear polarised light is no longer rotated in the dielectric (the liquid crystal is uniaxially perpendicular to the surface of the plates). This effect is reversible and can be used for electrically controlling the optical transmissivity of the condenser.

In such "light rotation cells" it is desirable to use compounds which possess a low melting point and a slight viscosity. It has now been surprisingly found in accordance with the present invention that the compounds of formula I hereinbefore possess liquid crystalline properties which correspond to the foregoing requirements. They exhibit not only the necessary large positive anistropy of the dielectric constants but also individually or

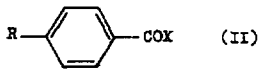
in the form of mixtures with one another or with other nematic or non-nematic substances, they are liquid crystalline and exhibit a slight viscosity at relatively low temperature. The operation of electro-optical devices is therefore possible with lower voltage and the susceptibility is shorter. An advantage of the compounds of formula I over compounds formerly used for this purpose is their much greater stability which enables them to be handled more conveniently. A further advantage of the compounds of formula I is that they form colourless, milky-white nematic phases.

The compounds of formula I are preferably used in the form of mixtures with one another or with other nematic or non-nematic substances. Binary or ternary mixtures can be formed. Mixtures whose composition corresponds to a eutectic are especially preferred.

More especially preferred are mixtures of *p* - n - heptylbenzoic acid *p'*-cyanophenyl ester with *p* - n - butylbenzoic acid *p'*-cyanophenyl ester or *p* - n - pentylbenzoic acid *p'*-cyanophenyl ester in a molar ratio of 2:1, *p* - n - octylbenzoic acid *p'*-cyanophenyl ester with *p* - n - butylbenzoic acid *p'*-cyanophenyl ester or *p* - n - hexylbenzoic acid *p'*-cyanophenyl ester in a molar ratio 2:1 or *p* - n - hexylbenzoic acid *p'*-cyanophenyl ester with *p* - n - butylbenzoic acid *p'*-cyanophenyl ester in a molar ratio of 2:1.

The compounds of formula I hereinbefore can be manufactured in accordance with the process provided by the present invention by

a) reacting a compound of the general formula

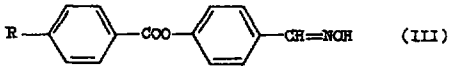


(II)

wherein R has the significance given earlier and X represents a leaving atom or group, with p-hydroxybenzonitrile,

or

b) dehydrating a compound of the general formula

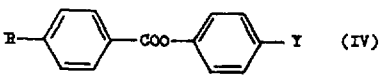


(III)

wherein R has the significance given earlier, at the reflux temperature of the mixture,

or

c) reacting a compound of the general formula



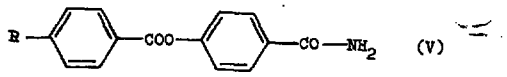
(IV)

wherein R has the significance given earlier and Y represents a halogen atom or an arylsulphonyloxy group,

with cuprous cyanide or sodium cyanide,

or

d) dehydrating a compound of the general formula

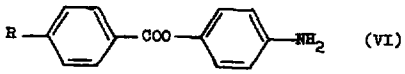


(V)

wherein R has the significance given earlier, at atmospheric pressure or at a reduced pressure,

or

e) diazotising a compound of the general formula



(VI)

wherein R has the significance given earlier, in water at a temperature of 0°—5°C with the addition of hydrochloric acid and sodium nitrite, and reacting the diazonium salt obtained with cuprous cyanide.

The leaving atom or group denoted by X in formula II can be a halogen atom or a lower alkoxy (preferably methoxy or ethoxy), lower alkanoyloxy (preferably formyloxy or acetoxy), aryl-(lower alkoxy) (preferably benzyloxy), aryl-(lower alkanoyloxy) (preferably benzoyloxy), lower alkylsulphonyloxy (preferably tosyloxy) or arylsulphonyloxy (preferably tosyloxy) group. The word "lower" is used herein to denote a radical (unbranched or branched) containing up to 7 carbon atoms.

In embodiment a) of the process in accordance with the present invention a compound of formula II is reacted with *p*-hydroxybenzonitrile. This reaction is expediently carried out in an inert organic solvent such as, for example, an ether (e.g. diethyl ether or tetrahydrofuran) or dimethylformamide, benzene, toluene, cyclohexane or carbon tetrachloride.

In the compounds of formula II, X preferably represents a halogen atom, especially a chlorine atom. In order to bind the hydrogen halide released during the reaction, an acid binding agent is expediently present in the reaction mixture. Suitable acid binding agents are tertiary amines and pyridine. The acid binding agent is preferably present in a large excess so that it can serve simultaneously as a solvent and acid binding agent. The temperature and pressure are not critical aspects of this reaction. However, the reaction is generally carried out at atmospheric pressure and at a temperature between room temperature and the boiling temperature of the reaction mixture.

The compounds of formula II in which X represents a chlorine atom can be prepared by reacting a corresponding benzoic acid with thionyl chloride. It is not necessary to isolate

such a compound of formula II from the mixture in which it is prepared prior to the reaction with *p*-hydroxybenzonitrile.

In embodiment b) of the process in accordance with the invention a compound of formula III is dehydrated. The dehydration is expediently carried out using acetic anhydride or anhydrous sodium acetate in glacial acetic acid. As stated above, the dehydration is carried out at the reflux temperature of the mixture. The pressure is not critical, but the dehydration is advantageously carried out at atmospheric pressure.

The compounds of formula III can be prepared by reacting a compound of formula II with *p*-hydroxybenzaldehyde and reacting the resulting ester with hydroxylamine. A thus obtained compound of formula III need not be isolated from the mixture in which it is prepared, but can be dehydrated in situ.

In embodiment c) of the process in accordance with the present invention a compound of formula IV is reacted with cuprous cyanide or sodium cyanide. This reaction is expediently carried out in an inert organic solvent such as, for example, ethyleneglycol, tetrahydrofuran, dimethylformamide, dimethyl sulphoxide, pyridine or acetonitrile. The temperature and pressure are not critical aspects in this reaction. It is expedient to carry out the reaction at atmospheric pressure and at a temperature between room temperature and the boiling temperature of the reaction mixture.

In the compounds of formula IV, Y preferably represents a halogen atom, especially a bromine atom. Such compounds, which can be prepared, for example, by reacting a compound of formula II with *p*-bromophenol, need not be isolated from the reaction mixture, but can be reacted in situ with cuprous cyanide or sodium cyanide.

In embodiment d) of the process in accordance with the present invention a compound of formula V is dehydrated. The dehydration can be carried out by boiling a compound of formula V with acetic anhydride in glacial acetic acid or by using phosphorus pentoxide, phosphorus pentachloride, phosphorus oxychloride or thionyl chloride. This dehydration is preferably carried out in the absence of a solvent but where a solvent is used suitable solvents are, for example, benzene, dimethylformamide, pyridine and ethylene dichloride. The dehydration is advantageously carried out at the reflux temperature of the mixture or the boiling point of the product. As stated above, the dehydration is carried out at atmospheric pressure or at a reduced pressure.

The compounds of formula V can be prepared by reacting a compound of formula II with *p*-hydroxybenzoic acid, converting the product into an acid chloride and treating this with ammonia. The compounds of formula V need not be isolated from the mixture in which they are prepared, but can be dehydrated in situ.

In embodiment e) of the process in accordance with the present invention a compound of formula VI is used as the starting material and is expediently diazotised and the resulting diazonium salt is subjected to a Sandmeyer reaction. As stated above, the diazotisation is carried out in water at a temperature of 0°—5°C with the addition of hydrochloric acid and sodium nitrite. The diazonium chloride obtained is then subjected to a Sandmeyer reaction. This reaction is expediently carried out using a solution of, for example, cuprous cyanide or a complex salt thereof. This reaction is preferably carried out at a temperature between 0°C and 100°C, and more preferably at between 70° and 80°C. The pressure is not critical, but the reaction is advantageously carried out at atmospheric pressure.

The compounds of formula VI can be prepared by reacting a compound of formula II with N - benzylidene - *p* - hydroxyaniline and subsequent cleavage of the resulting Schiff's base with an aqueous mineral acid.

The physical properties of the nematic compounds of formula I provided by the present invention are given in the following Table:

TABLE

	R	M.p.	Cl.p.
A	n-butyl	67°C	(41.5°C)*
B	n-pentyl	60.5°C	(56.5°C)*
C	n-hexyl	45°C	48°C
D	n-heptyl	44°C	56.5°C
E	n-octyl	46.5°C	53.5°C

* monotrope clearing point

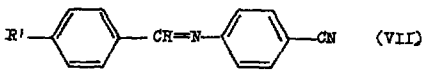
The compounds of formula I are preferably used in the form of mixtures with one another, with mixtures which correspond to a eutectic being especially preferred.

Examples of some mixtures are given in the following Table:

TABLE

Mixture	M.p.	Cl.p.
67% D + 33% A	24° – 26°C	50°C
67% D + 33% B	30° – 30.5°C	56°C
67% E + 33% A	22° – 24°C	48.5°C
67% E + 33% C	22° – 23°C	51°C
67% C + 33% A	22° – 23°C	45° – 45.5°C

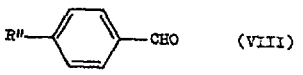
The compounds of formula I can also be used in the form of mixtures with other nematic or non-nematic substances such as, for example, with Schiffs' bases of the general formula



(VII)

wherein R' represents a straight-chain alkyl group containing 2 to 8 carbon atoms, a straight-chain alkoxy group containing 4 to 7 carbon atoms or a straight-chain alkanoyloxy group containing 2 to 8 carbon atoms.

The Schiffs' bases of formula VII in which R' represents a straight-chain alkyl group containing 2 to 8 carbon atoms are described and claimed in our Application No. 9051/73 (Serial No. 1373609) and can be prepared, for example, by reacting a compound of the general formula



(VIII)

wherein R'' represents a straight-chain alkyl group containing 2 to 8 carbon atoms, with *p*-aminobenzonitrile.

The following Examples illustrate the process provided by the present invention:

Example 1.

5.6 g (28.5 mmol) of *p* - n -butylbenzoic acid chloride in 12 ml of absolute benzene are added to 3.1 g (26 mmol) of *p*-hydroxybenzonitrile in 25 ml of absolute pyridine. The mixture is stirred overnight at room temperature and subsequently for a further 2 hours at 50°C. After cooling, the mixture is extracted with ether and the extract washed with dilute hydrochloric acid and water. There are finally obtained 9 g of crude *p* - n - butylbenzoic acid *p'*-cyanophenyl ester. This crude product is dissolved in toluene and chromatographed on 250 g of silica gel. From the uniform fraction in the thin-layer there are obtained, after recrystallization from hexane, 4 g of product of melting point 67°C (monotrope clearing point 41.5°C). The nuclear magnetic resonance and infrared spectra correspond to the expected structure.

The starting material can be prepared as follows:

50 g of *p* - n - butylbenzoic acid are dissolved in 150 ml of thionyl chloride and the mixture is boiled under reflux for 1 hour. The excess thionyl chloride is then removed at normal pressure and the *p* - n - butylbenzoic acid chloride distilled under a high vacuum. The acid chloride has a boiling point of 100°—105°C/2—5 mm.

Example 2.

3.1 g (26 mmol) of *p*-hydroxybenzonitrile are dissolved in 40 ml of absolute pyridine. Then 6 g (28.5 mmol) of *p* - n - pentylbenzoic acid chloride in 20 ml of benzene are added dropwise at room temperature and the mixture is subsequently stirred overnight. After warming for a short period, the mixture is worked up as described in Example 1 and there are thus obtained 7.5 g of crude ester. This is chromatographed on silica gel using toluene/acetone (19:1). From the uniform fraction there are obtained, after recrystallisation from hexane, 2.6 g of *p* - n - pentylbenzoic acid *p'*-cyanophenyl ester of melting point 60.5°C and a monotrope clearing point of 56.5°C.

The starting material can be prepared as follows:

15 g of *p* - n - pentylbenzoic acid are dissolved in 100 ml of thionyl chloride and the mixture is boiled under reflux for 1 hour.

The excess thionyl chloride is then removed by distillation and the desired acid chloride distilled under a high vacuum. The acid chloride has a boiling point of 104°C/2 mm.

Example 3.

1.5 g (11.75 mmol) of *p*-hydroxybenzonitrile in 25 ml of absolute pyridine and 2.9 g (13 mmol) of *p* - n - hexylbenzoic acid chloride in 12 ml of absolute benzene are mixed together, stirred overnight at room temperature and subsequently for a further 2 hours at 50°C. The cooled reaction mixture is poured on to ice-water and then extracted with ether. The mixture is washed with dilute hydrochloric acid, dilute sodium hydroxide and finally with water until neutral. After drying and concentration of the solution, there are obtained 3.7 g of crude product which is firstly chromatographed on silica gel using toluene/acetone (19:1). There are finally obtained 1.4 g of *p* - n - hexylbenzoic acid *p'*-cyanophenyl ester of melting point 45°C; clearing point 48°C.

The starting material can be prepared as follows:

9.4 g of *p* - n - hexylbenzoic acid and 50 ml of thionyl chloride are mixed together and warmed for 1 hour at 80°C. The excess thionyl chloride is then distilled off at normal pressure and then the *p* - n - hexyl benzoic acid chloride is distilled off under a high vacuum. The acid chloride has a boiling point of 110°C/0.05 mm.

Example 4.

6.6 g (28 mmol) of *p* - n - heptylbenzoic acid chloride are dissolved in 25 ml of absolute benzene and added dropwise to 3 g (25 mmol) of *p*-hydroxybenzonitrile in 50 ml of absolute pyridine. The reaction mixture is stirred overnight at room temperature and then for a further 2 hours at 50°C. After cooling, ice-water is added and the product is extracted with ether. The extract is washed with dilute hydrochloric acid, dilute sodium hydroxide and water and there are finally obtained 7.6 g of crude *p* - n - heptylbenzoic acid *p'*-cyanophenyl ester. This is chromatographed on 300 g of silica gel and eluted with hexane/ether (4:1). After recrystallisation from hexane, 6.0 g of the desired product are obtained; melting point 44°C and clearing point 56.5°C.

The starting material can be prepared as follows:

15 g of *p* - n - heptylbenzoic acid and 100 ml of thionyl chloride are boiled under reflux until the evolution of gas has terminated. The excess thionyl chloride is then distilled off at normal pressure and the *p* - n - heptylbenzoic acid chloride is distilled under a high vacuum. 13.2 g of acid chloride of boiling point 165°—167°C/5 mm are obtained.

Example 5.

7 g (27.5 mmol) of *p* - n -octylbenzoic acid chloride in 25 ml of absolute benzene are added dropwise to 3 g (25 mmol) of *p*-hydroxybenzonitrile in 50 ml of absolute pyridine. The mixture is then stirred overnight at room temperature and for a further 2 hours at 50°C. The reaction mixture is poured on to ice-water and the product isolated as described in Example 4. 8.7 g of crude ester are chromatographed on silica gel using benzene. There are obtained, after recrystallisation from hexane, 5.2 g of pure *p* - n - octylbenzoic acid *p'*-cyanophenyl ester of melting point 46.5°C and clearing point 53.5°C.

The starting material can be prepared as follows:

20 g of *p* - n - octylbenzoic acid and 100 ml of thionyl chloride are boiled under reflux for 1 hour. The excess thionyl chloride is distilled off at normal pressure, the residue mixed with absolute toluene and concentrated under a vacuum. The crude *p* - n - octylbenzoic acid chloride can be used without further purification.

Example 6.

4.5 g (37 mmol) of *p*-hydroxybenzaldehyde are dissolved in 50 ml of pyridine. 8 g (40.5 mmol) of *p* - n - butylbenzoic acid chloride in 25 ml of benzene are added dropwise thereto at room temperature. The mixture is stirred overnight at room temperature and subsequently for a further 2 hours at 50°C. The mixture is then poured on to ice-water and extracted with ether. The extract is washed with water, dilute hydrochloric acid and water and there are finally obtained, after drying and concentration of the solution, 10.2 g of crude ester. 8.2 g of crystalline ester are obtained after recrystallisation from ether/hexane. 8 g (27.5 mmol) of this ester are boiled under reflux for 16 hours with 2.85 g (41 mmol) of hydroxylamine hydrochloride and 4.5 g (55 mmol) of anhydrous sodium acetate in 100 ml of glacial acetic acid. The mixture is cooled, the major amount of the glacial acetic acid distilled off under a vacuum, water added to the residue and the product extracted with ether. From the extract there are obtained after washing with water and drying with sodium sulphate, 7.0 g of crude product. This is chromatographed on silica gel using benzene. From the uniform fractions there are obtained, after recrystallization from hexane, *p* - n - butylbenzoic acid *p'*-cyanophenyl ester which is identical with that obtained in Example 1.

Example 7.

3.7 g (9.5 mmol) of *p* - n - octylbenzoic acid *p'*-bromophenyl ester are boiled under reflux with 1.1 g (12.5 mmol) of cuprous cyanide in 5 ml of dimethylformamide. The

reaction mixture is then poured on to 2 ml of ethylenediamine and 6 ml of water, shaken vigorously for 5 minutes and then extracted twice with benzene. The organic extracts are washed again with ethylenediamine in water and then several times with water. 1.9 g of crystalline crude product are obtained, but this still contains a small amount of starting material which is separated by chromatography on silica gel using toluene. The *p* - n - octylbenzoic acid *p'*-cyanophenyl ester obtained by recrystallisation has a melting point of 46.5°C and a clearing point of 54°C and is identical with the product obtained in Example 5.

The starting material can be prepared as follows:

4.5 g (26 mmol) of *p*-bromophenyl are dissolved in 50 ml of absolute pyridine and mixed with 7 g (28 mmol) of *p* - n - octylbenzoic acid chloride in 25 ml of absolute benzene. The mixture is subsequently stirred overnight at room temperature, then poured into ice-water and extracted with ether. The organic phase is washed with dilute hydrochloric acid, dilute sodium hydroxide and water, dried over sodium sulphate and concentrated. There are obtained 8.4 g of *p* - n - octylbenzoic acid *p'*-bromophenyl ester which is practically pure in the thin-layer.

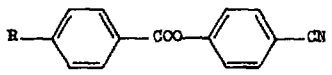
The following Example illustrates the preparation of a Schiff's base of formula VII hereinbefore:

Example A.

A mixture of 5.9 g (0.05 mol) of *p*-aminobenzonitrile and 6.7 g (0.05 mol) of *p*-ethylbenzaldehyde is gassed with nitrogen in 100 ml of benzene after the addition of 150 mg of *p*-toluenesulphonic acid and the mixture is heated under reflux for 1 hour (bath temperature 120°C). The water formed is removed by means of a water separator. During a further hour, the benzene condensed in the reflux condenser is led back into the reaction vessel via a layer of 50 g of aluminium oxide (activity I). After cooling, 2 g of solid potassium carbonate are added, the mixture is filtered and the filtrate freed from solvent in a vacuum at 50°C (bath temperature). There remain behind 11.5 g of a yellow oil which crystallises upon cooling. Purification is carried out by several recrystallisations from isopropanol up to constant melting point and until byproducts can no longer be observed in the gas chromatogram. The pure *p* - [(*p* - ethylbenzylidene)amino]benzonitrile melts at 76.2°—77.0°C and is liquid crystalline upon cooling to 63.0°—59.7°C; U.V. (ethanol): $\varepsilon_{277}=25800$ (shoulder at 316 nm). The nuclear magnetic resonance, mass spectrum, infrared and microanalysis confirm the structure of the product.

WHAT WE CLAIM IS:—

1. A compound of the general formula



(I)

wherein R represents a straight-chain alkyl group containing 4 to 8 carbon atoms.

2. *p* - n - Butylbenzoic acid *p'*-cyanophenyl ester.

3. *p* - n - Pentylbenzoic acid *p'*-cyanophenyl ester.

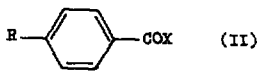
4. *p* - n - Hexylbenzoic acid *p'*-cyanophenyl ester.

5. *p* - n - Heptylbenzoic acid *p'*-cyanophenyl ester.

6. *p* - n - Octylbenzoic acid *p'*-cyanophenyl ester.

7. A process for the manufacture of the compounds of formula I given in claim 1, which process comprises

a) reacting a compound of the general formula



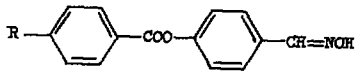
(II)

wherein R has the significance given in claim 1 and X represents a leaving atom or group,

with *p*-hydroxybenzonitrile,

or

b) dehydrating a compound of the general formula

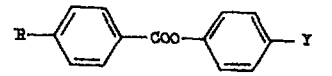


(III)

wherein R has the significance given in claim 1, at the reflux temperature of the mixture,

or

c) reacting a compound of the general formula



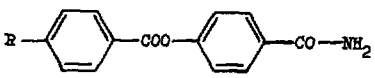
(IV)

wherein R has the significance given in claim 1 and Y represents a halogen atom or an arylsulphonyloxy group,

with cuprous cyanide or sodium cyanide,

or

d) dehydrating a compound of the general formula



(V)

reaction mixture is then poured on to 2 ml of ethylenediamine and 6 ml of water, shaken vigorously for 5 minutes and then extracted twice with benzene. The organic extracts are washed again with ethylenediamine in water and then several times with water. 1.9 g of crystalline crude product are obtained, but this still contains a small amount of starting material which is separated by chromatography on silica gel using toluene. The *p* - n - octylbenzoic acid *p'*-cyanophenyl ester obtained by recrystallisation has a melting point of 46.5°C and a clearing point of 54°C and is identical with the product obtained in Example 5.

The starting material can be prepared as follows:

4.5 g (26 mmol) of *p*-bromophenyl are dissolved in 50 ml of absolute pyridine and mixed with 7 g (28 mmol) of *p* - n - octylbenzoic acid chloride in 25 ml of absolute benzene. The mixture is subsequently stirred overnight at room temperature, then poured into ice-water and extracted with ether. The organic phase is washed with dilute hydrochloric acid, dilute sodium hydroxide and water, dried over sodium sulphate and concentrated. There are obtained 8.4 g of *p* - n - octylbenzoic acid *p'*-bromophenyl ester which is practically pure in the thin-layer.

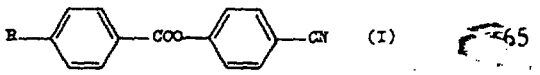
The following Example illustrates the preparation of a Schiff's base of formula VII hereinbefore:

Example A.

A mixture of 5.9 g (0.05 mol) of *p*-aminobenzonitrile and 6.7 g (0.05 mol) of *p*-ethylbenzaldehyde is gassed with nitrogen in 100 ml of benzene after the addition of 150 mg of *p*-toluenesulphonic acid and the mixture is heated under reflux for 1 hour (bath temperature 120°C). The water formed is removed by means of a water separator. During a further hour, the benzene condensed in the reflux condenser is led back into the reaction vessel via a layer of 50 g of aluminium oxide (activity I). After cooling, 2 g of solid potassium carbonate are added, the mixture is filtered and the filtrate freed from solvent in a vacuum at 50°C (bath temperature). There remain behind 11.5 g of a yellow oil which crystallises upon cooling. Purification is carried out by several recrystallisations from isopropanol up to constant melting point and until byproducts can no longer be observed in the gas chromatogram. The pure *p* - [(*p* - ethylbenzylidene)amino]benzonitrile melts at 76.2°—77.0°C and is liquid crystalline upon cooling to 63.0°—59.7°C; U.V. (ethanol): $\varepsilon_{317}=25800$ (shoulder at 316 nm). The nuclear magnetic resonance, mass spectrum, infrared and microanalysis confirm the structure of the product.

WHAT WE CLAIM IS:—

1. A compound of the general formula



(I)

wherein R represents a straight-chain alkyl group containing 4 to 8 carbon atoms.

2. *p* - n - Butylbenzoic acid *p'*-cyanophenyl ester.

3. *p* - n - Pentylbenzoic acid *p'*-cyanophenyl ester.

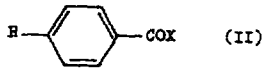
4. *p* - n - Hexylbenzoic acid *p'*-cyanophenyl ester.

5. *p* - n - Heptylbenzoic acid *p'*-cyanophenyl ester.

6. *p* - n - Octylbenzoic acid *p'*-cyanophenyl ester.

7. A process for the manufacture of the compounds of formula I given in claim 1, which process comprises

a) reacting a compound of the general formula



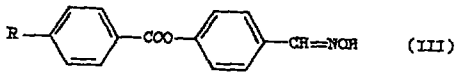
(II)

wherein R has the significance given in claim 1 and X represents a leaving atom or group,

with *p*-hydroxybenzonitrile,

or

b) dehydrating a compound of the general formula

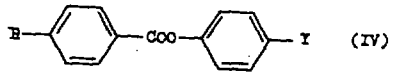


(III)

wherein R has the significance given in claim 1, at the reflux temperature of the mixture,

or

c) reacting a compound of the general formula



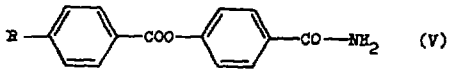
(IV)

wherein R has the significance given in claim 1 and Y represents a halogen atom or an arylsulphonyloxy group,

with cuprous cyanide or sodium cyanide,

or

d) dehydrating a compound of the general formula



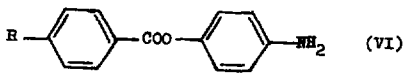
(V)

* C L M S *

wherein R has the significance given in claim 1, at atmospheric pressure or at a reduced pressure,

or

e) diazotising a compound of the general formula



(VI)

wherein R has the significance given in claim 1, in water at a temperature of 0°—5°C with the addition of hydrochloric acid and sodium nitrite,

and reacting the diazonium salt obtained with cuprous cyanide.

8. A process according to claim 7, wherein *p* - n - butylbenzoic acid *p'*-cyanophenyl ester is manufactured.

9. A process according to claim 8, wherein *p* - n - butylbenzoic acid chloride is reacted with *p*-hydroxybenzonitrile or *p* - n - butylbenzoic acid and *p'*-oximinophenyl ester is dehydrated.

10. A process according to claim 7, wherein *p* - n - pentylbenzoic acid *p'*-cyanophenyl ester is manufactured.

11. A process according to claim 10, wherein *p* - n - pentylbenzoic acid chloride is reacted with *p*-hydroxybenzonitrile.

12. A process according to claim 7, wherein *p* - n - hexylbenzoic acid *p'*-cyanophenyl ester is manufactured.

13. A process according to claim 12, wherein *p* - n - hexylbenzoic acid chloride is reacted with *p*-hydroxybenzonitrile.

14. A process according to claim 7, wherein *p* - n - heptylbenzoic acid *p'*-cyanophenyl ester is manufactured.

15. A process according to claim 14, wherein *p* - n - heptylbenzoic acid chloride is reacted with *p*-hydroxylbenzonitrile.

16. A process according to claim 7, wherein *p* - n - octylbenzoic acid *p'*-cyanophenyl ester is manufactured.

17. A process according to claim 16, wherein *p* - n - octylbenzoic acid is reacted with *p*-hydroxybenzonitrile or *p* - n - octylbenzoic acid *p'*-bromophenyl ester is reacted with cuprous cyanide.

18. A process for the manufacture of the compounds of formula I given in claim 1, substantially as hereinbefore described with reference to Examples 1 to 7.

19. Compounds of formula I given in claim 1, when manufactured by the process claimed in any one of claims 7 to 18 inclusive.

20. A nematic mixture for electro-optical purposes which consists of a mixture of compounds of formula I given in claim 1 with one another and/or with other nematic substances and/or with non-nematic substances.

21. A nematic mixture according to claim 20 which consists of a mixture of *p* - n - heptylbenzoic acid *p'*-cyanophenyl ester and *p* - n - butylbenzoic acid *p'*-cyanophenyl ester.

22. A nematic mixture according to claim 20 which consists of a mixture of *p* - n - heptylbenzoic acid *p'*-cyanophenyl ester and *p* - n - pentylbenzoic acid *p'*-cyanophenyl ester.

23. A nematic mixture according to claim 20 which consists of a mixture of *p* - n - octylbenzoic acid *p'*-cyanophenyl ester and *p* - n - butylbenzoic acid *p'*-cyanophenyl ester.

24. A nematic mixture according to claim 20 which consists of a mixture of *p* - n - octylbenzoic acid *p'*-cyanophenyl ester and *p* - n - hexylbenzoic acid *p'*-cyanophenyl ester.

25. A nematic mixture according to claim 20 which consists of a mixture of *p* - n - hexylbenzoic acid *p'*-cyanophenyl ester and *p* - n - butylbenzoic acid *p'*-cyanophenyl ester.

26. A process for the production of nematic mixtures, which process comprises mixing compounds of formula I given in claim 1 with one another and/or with other nematic substances and/or non-nematic substances.

27. A process according to claim 26 wherein *p* - n - heptylbenzoic acid *p'*-cyanophenyl ester is mixed with *p* - n - butylbenzoic acid *p'*-cyanophenyl ester.

28. A process according to claim 26, wherein *p* - n - heptylbenzoic acid *p'*-cyanophenyl ester is mixed with *p* - n - pentylbenzoic acid *p'*-cyanophenyl ester.

29. A process according to claim 26, wherein *p* - n - octylbenzoic acid *p'*-cyanophenyl ester is mixed with *p* - n - butylbenzoic acid *p'*-cyanophenyl ester.

30. A process according to claim 26, wherein *p* - n - octylbenzoic acid *p'*-cyanophenyl ester is mixed with *p* - n - hexylbenzoic acid *p'*-cyanophenyl ester.

31. A process according to claim 26, wherein *p* - n - hexylbenzoic acid *p'*-cyanophenyl ester is mixed with *p* - n - butylbenzoic acid *p'*-cyanophenyl ester.

32. A dielectric for electro-optical purposes containing a compound of formula I given in claim 1 in liquid crystalline form.

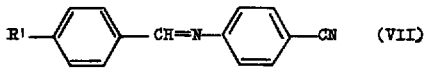
33. A dielectric for electro-optical purposes containing a compound of formula I as claimed in any one of claims 2 to 6 inclusive, in liquid crystalline form.

34. A dielectric for electro-optical purposes consisting of a nematic mixture as claimed in any one of claims 20 to 25 inclusive.

35. A process for the production of a dielectric usable for electro-optical purposes, which process comprises using a nematic compound of formula I given in claim 1 or a mixture of such compounds with one another and/or with other nematic substances and/or with non-nematic substances.

36. A process according to claim 35, wherein a mixture of compounds of formula I with one another is used.

37. A process according to claim 35, wherein a mixture of a compound of formula I with a Schiff's base of the general formula



(VII)

wherein R' represents a straight-chain alkyl group containing 2 to 8 carbon atoms, a straight-chain alkoxy group containing 4 to 7 carbon atoms or a straight-chain alkanoyloxy group containing 2 to 8 carbon atoms, is used.

38. A process according to claim 35 or claim 36, wherein a mixture of *p* - n - heptylbenzoic acid *p'*-cyanophenyl ester with *p* - n - butylbenzoic acid *p'*-cyanophenyl ester is used.

39. A process according to claim 35 or claim 36, wherein a mixture of *p* - n - heptylbenzoic acid *p'*-cyanophenyl ester with *p* - n - pentylbenzoic acid *p'*-cyanophenyl ester is used.

40. A process according to claim 35 or claim 36, wherein a mixture of *p* - n - octylbenzoic acid *p'*-cyanophenyl ester with *p* - n - butylbenzoic acid *p'*-cyanophenyl ester is used.

41. A process according to claim 35 or claim 36, wherein a mixture of *p* - n - octylbenzoic acid *p'*-cyanophenyl ester with *p* - n - hexylbenzoic acid *p'*-cyanophenyl ester is used.

42. A process according to claim 35 or claim 36, wherein a mixture of *p* - n - hexylbenzoic acid *p'*-cyanophenyl ester with *p* - n - butylbenzoic acid *p'*-cyanophenyl ester is used.

For the Applicants,
CARPMAELS & RANSFORD,
Chartered Patent Agents,
43 Bloomsbury Square,
London WC1A 2RA.

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